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A New Commercializable Route for the Preparation of Single-Source Precursors for Bulk, Thin-Film, and Nanocrystallite I-III-IV Semiconductors

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July 2004

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A New Commercializable Route for the Preparation of Single-Source Precursors for Bulk, Thin-Film, and Nanocrystallite I-III-VI Semiconductors

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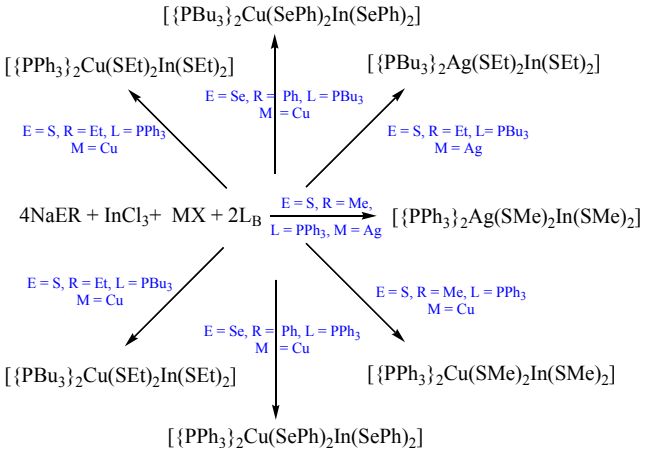
We report a new simplified synthetic procedure for commercial manufacture of ternary single source precursors (SSP). This new synthetic process has been successfully implemented to fabricate known SSPs on bulk scale and the first liquid SSPs to the semiconductors $CuInSe_2$ and $AgIn_xS_y$. Single crystal x-ray determination reveals the first unsolvated ternary AgInS SSP. SSPs prepared via this new route have successfully been used in a spray assisted chemical vapor deposition (CVD) process to deposit polycrystalline thin films, and for preparing ternary nanocrystallites.

Although SSP CVD precursors may be highly efficient for their intended application, their use has historically been limited to the lab and their full potential never exploited. This is primarily due to the cumbersome, or lengthy synthetic methodology and the need to employ expensive and/or non-commodity starting reagents. Thus, a key point in designing a new CVD precursor for commercialization is one that avoids these pitfalls. Our team of NASA Glenn Research Center and external collaborators has been actively involved for the past decade on binary and polyatomic precursors for the fabrication of thin-film semiconducting layers.[1] Throughout the course of the program, materials of the type $[\{L\}_xM^{(I)}(\mu\text{-}ER)_2M^{(III)}(ER)_2]$, (L = Lewis base, M = transition /main group metal, E = Grp VI and R = organic moiety) have been developed.[2] We have further developed and successfully shown SSPs based on this architecture to be excellent candidates for depositing I-III-VI_2 type semiconductors,[3–7] which have been established as a key material for the fabrication of the next generation photovoltaic (PV) devices. For example, current solar cells based on $CuInS_2$ and $Cu(Ga:In)Se_2$ have demonstrated efficiencies of 12.5 and 18.8 percent, respectively.[8,9] Furthermore, the importance of ternary SSPs is exemplified by a renewed interest by groups designing SSPs to ternary chalcogenide semiconductors.[10,11]

The current *U.S. Photovoltaic Roadmap* indicates the importance of developing new commercial processes for polycrystalline thin-film solar cells.[12] Current methods for the synthesis of $[\{L\}_xM^{(I)}(\mu\text{-}ER)_2M^{(III)}(ER)_2]$ SSPs, can be lengthy and require the use of non-bulk commodity starting materials.[1,2] In attempting to make these SSPs commercially viable candidates for large-scale thin-film processes, we have devised a new simple synthetic route that employs commercially available reagents while retaining the flexibility for molecular engineering.

The SSPs are prepared by a "one-pot" type reaction as illustrated in scheme 1.

Initial investigations were conducted for the preparation of the known SSP $[\{PPh_3\}_2Cu(\mu\text{-}SEt)_2In(SEt)_2]$,[2] to the semiconductor $CuInS_2$. Under anaerobic conditions, $InCl_3$ is reacted with sodium ethanethiolate in methanol in a 1:4 ratio to afford the ionic stable intermediate $Na^+[In(SEt)_4]^-$. After approximately 15 minutes, a solution of CuCl and the Lewis base in CH_3CN/CH_2Cl_2 is added directly to the



Scheme 1. New preparative route to Ternary I-III-IV SSPs.

freshly prepared $Na^+[In(SEt)_4]^-$. After 24 hours the reaction is essentially complete. Concentration of the methanolic solution and extraction of the product with CH_2Cl_2, followed by washing with dry ether and pentane affords a creamy white solid. NMR and elemental analysis confirmed the product to be $[\{PPh_3\}_2Cu(\mu\text{-}SEt)_2In(SEt)_2]$ **1**. The flexibility of the new synthetic procedure to permit tailoring of the SSPs was also examined. Using a similar synthetic procedure to that outlined above, the ternary SSP **2** (L = PPh_3, E = Se, R = Ph), **3** (L = PBu_3, E = S, R = Et) and the new SSP **4** (L = PPh_3, E = S, R = Me), and **5** (L = PBu_3, E = Se, R = Ph) were also prepared in good yields (>85 percent). The versatility of the route was further examined by preparing two new analogous silver ternary SSPs **6** $[\{PPh_3\}_2Ag(\mu\text{-}SMe)_2In(SMe)_2]$ and **7** $[\{PBu_3\}_2Ag(\mu\text{-}SEt)_2In(SEt)_2]$. After 24 hours, the products are extracted as crystalline materials from CH_2Cl_2, or in the case of **3, 5** as yellow and **7** as clear liquids from pentane. Thus, SSPs **5** and **7** represent the first liquid precursors to polycrystalline $AgIn_xS_y$ and $CuInSe_2$ type semiconductors. Spectroscopic, thermal, and elemental analyses confirm the formation and purity of the products (see supporting info).

The key to the new preparative route is that the M^+ cations are very effectively solvated by MeCN, due to the high formation constants of M-NR type complexes.[13] This facilitates the formation of the desired stable tetrahedral intermediate $[M(CH_3CN)_4]^+X$ *in situ*. With the successive addition of the chosen Lewis base, the first "half" of the molecule $[\{L\}_xM(CH_3CN)_{4-x}]^+X$, is constructed with ease and importantly without the need for detailed Schlenk techniques. Through experimental studies, SSPs have been prepared in yields >85 percent on 40 mmol scale (>30 g), thus making the procedure very attractive for

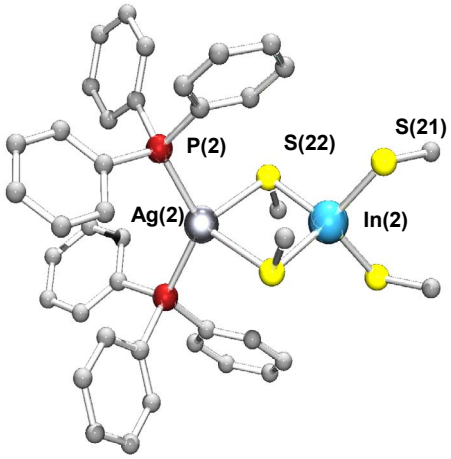


Figure 1. Single crystal x-ray Pluto representation of SSP **6**.[14] Selected bond distances (Å) and angles (deg°): Ag(2)–P(2) 2.4527(10), Ag(2)–S(22) 2.6797(10), In(2)–S(21) 2.4333(11), In(2)–S(22) 2.4841(11), P(2)–Ag(2)–P(2) 128.40(5), P(2)–Ag(2)–S(22) 112.32(3), S(22)–Ag(2)–S(22) 91.03(5), In(2)–S(22)–Ag(2) 84.16(3), S(21)–In(2)–S(21) 108.91(5).

mass production. Crystals of SSP **6** suitable for single-crystal x-ray diffraction studies, obtained by controlled growth from a biphasic solvent system of CH_2Cl_2/ Hexane at room temperature overnight led to the determination of its crystal structure, figure 1.

The structure is tetrahedral with respect to both the silver and indium metal centers, which are connected via two bridging methylthiolato groups, and is unique since it is the first representation of an unsolvated ternary $AgIn_xS_y$ structure of this type. Examination of the bond lengths and angles shows that they are generally unexceptional. The Ag-P distance (2.453 Å) is representative of the sum of the single bond covalent radii (2.44 Å). The P–Ag–P angle is known to vary considerably (e.g., 113 to 138.26°), depending on the steric and electronic properties of peripheral groups.[15] This is clearly evident, since the P–Ag–P angle of 128.41° is greater than that of 122.44° reported by Vittal and O'Brien,[11] where they report a $CHCl_3$ solvated structure with the sterically more demanding benzylthiocarboxylate group. Furthermore, the limited steric encumbrance of the $^-$SMe group to the thiocarboxylate ligand is reflected in the smaller bond angles and length of the AgSInS cubane.

To demonstrate the utility of these advanced materials for fabricating I-III-VI_2 amorphous semiconductors, thin-films were grown in a spray CVD process. Films were frequently grown either at 760 or 30 mm Hg. The thickness of a typical film ranged from 0.75 to 1.0 µm, with grain size of approximately 0.5 µm. A more in-depth study of film morphology and deposition is addressed elsewhere.[7]

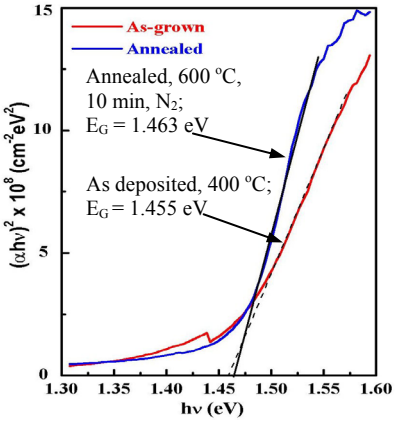


Figure 2. Band gap determination for $CuInS_2$ films using SSP **3**.[16]

Optical (fig. 2) and x-ray spectroscopic studies of the thin films deposited using the SSP synthesized via the new route were performed. Using SSP **3**, thin $CuInS_2$ films deposited at (400 °C/30 mm Hg) afforded near 1:1:2 stoichometry, which were 112 orientated (see supporting info). Rapid thermal annealing (10 min/600 °C) was found to greatly improve the crystalline quality of the $CuInS_2$ phase, and not adversely affect the band-gap.

Interestingly, x-ray diffraction (XRD) (Cu Kα, 1.541 Å), and optical characterization of thin films grown using the new liquid AgInS SSP **7**, revealed that thin films of $AgIn_5S_8$ were deposited (figs. 3 and 4), even though calculation of the atomic molar residue from TGA and XRD experiments indicated pyrolysis of **7** to afford bulk $AgInS_2$. A recent CVD study by O'Brien and Vittal using a similar SSP also showed the formation of $AgIn_5S_8$ films.[11] In order to determine whether growth temperature was responsible for the change in stoichiometry, AgInS films where deposited at a range of temperatures from 350 to 450 °C. In each case crystalline $AgIn_5S_8$ thin films were obtained, thus indicating that substrate temperature was not a limiting factor. Further studies are underway to determine the equilibrium between $AgIn_5S_8$ and $AgInS_2$ thin film formation.

In preliminary CVD studies using liquid SSP **4** to the semiconductor $CuInSe_2$, amorphous thin films could be fabricated. Films deposited at 400 °C/30 mm Hg on Mo and glass showed they were 112 orientated and had near 1:1:2 Stoichiometry, figure 5. SSPs **1**, and **2** prepared via the new route were also used to successfully prepare ternary nanocrystallites of $CuInS_2$ and $CuInSe_2$. A detailed and complete study has been recently published.[17]

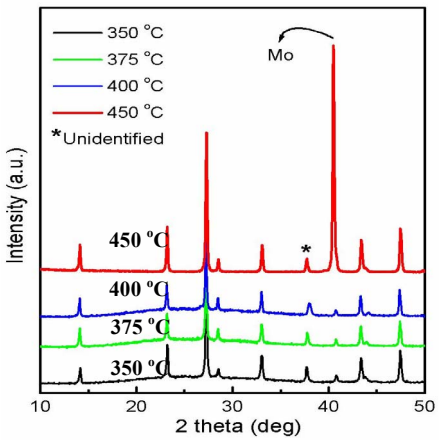


Figure 3. XRD spectra for as grown $AgIn_5S_8$ films on glass and Mo/glass, at reduced pressure, (30 mm Hg).

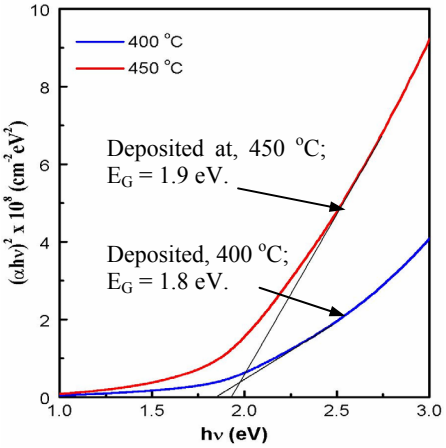


Figure 4. Band gap determination for as grown $AgIn_5S_8$ thin films, (E_G = 1.8 to 1.9) (30 mm Hg, liquid SSP **12**).[16]

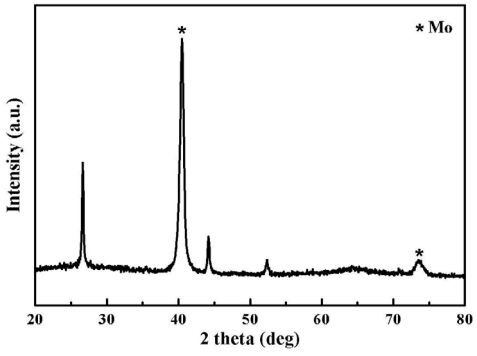


Figure 5. XRD of $CuInSe_2$ thin film on Mo 400 °C/30 mm Hg.

To summarize, the versatility of the new synthetic route for the preparation of known and new SSPs to multi-ternary semiconductors ([$\{LR_3\}_2M(\mu\text{–}ER')_2$ $M(ER')_2$]), is clearly demonstrated. This new synthetic route permits a simplified and easy method for fabricating SSPs without the need for non-commodity chemicals, or a detailed synthetic preparation. The new route retains flexibility, allowing full molecular engineering of the composition, stoichiometry and solid state-phase. This is shown by the preparation of the first liquid AgInS and $CuInSe_2$ SSPs, and the crystal structure determination of a unique un-solvated [$\{PPh_3\}_2Ag(\mu\text{-}SMe)_2In(SMe)_2$] complex. SSPs made via this new route have been successfully used to prepare ternary I-III-VI bulk materials, nanocrystallites, and thin films. Importantly, using ternary SSPs in a spray CVD process for semiconductor fabrication now establishes itself as a viable alternative to current methods of choice (co-evaporation of elementals) for fabricating I-III-VI_2 thin films for photovoltaic devices.

Supporting Information Available: Single-crystal x-ray bond length and angles (CIF), selective SEM, thermal, elemental analysis and spectroscopic data. This information is available free of charge via the internet at http://pubs.acs.org.

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Supporting Information

Crystal Data

Data Collection

A colorless plate of C40H42AgInP2S4 having approximate dimensions of 0.28×0.19×0.09 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 A) on a Nonius KappaCCD.

Cell constants and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 32849 reflections in the range $2 < \theta < 27°$. The monoclinic cell parameters and calculated volume are: a = 15.6671(4), b = 12.6092(4), c = 21.6432(8) A, β = 108.412(2)°, V = 4056.7(4)A^3. For Z = 4 and F.W. = 935.67, the calculated density is 1.53 g/cm^3. The refined mosaicity from DENZO/SCALEPACK was 0.37° indicating good crystal quality. The space group was determined by the program ABSEN (ref. 1). From the systematic presences of: h0l l = 2n and from subsequent least squares refinement, the space group was determined to be P2/c(# 13).

The data were collected at a temperature of 150 ±1. Data were collected to a maximum 2θ of 55.8°.

Data Reduction

A total of 32849 reflections were collected, of which 9649 were unique.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 13.4/cm for Mo K radiation. An empirical absorption correction using SCALEPACK (ref. 2) was applied. Transmission coefficients ranged from 0.725 to 0.890 with an average value of 0.851. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 8.7 percent based on intensity.

Structure Solution and Refinement

The structure was solved by direct methods using SIR97 (ref. 3). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full matrix least squares where the function minimized was Σw(|Fo|2 |Fc|2)2 and the weight w is defined as 1/[σ2(Fo2)+(0.0299P)2+0.0000P] where P=(Fo2+2Fc2)/3.

Scattering factors were taken from the "International Tables for Crystallography" (ref. 4). 9646 reflections were used in the refinements. However, only reflections with $Fo^2 > 2\sigma(Fo^2)$ were used in calculating R. The final cycle of refinement included 439 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.039$$
$$R2 = SQRT(\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2) = 0.076$$

The standard deviation of an observation of unit weight was 0.86. The highest peak in the final difference Fourier had a height of 1.03 e/A^3. The minimum negative peak had a height of 0.97 e/A^3.

Refinement was performed on a AlphaServer 2100 using SHELXL97 (ref. 5). Crystallographic drawings were done using programs ORTEP (ref. 6), and PLUTON (ref. 7).

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Single crystal x-ray data for $C_{40}H_{42}AgInP_2S_4$

Table of Bond Distances in Angstroms

Numbers in parentheses are estimated standard deviations in the least significant digits.

Atom 1	Atom 2	Distance
In(1)	S(11)	2.4273(11)
In(1)	S(11)	2.4273(11)
In(1)	S(12)	2.4797(10)
In(1)	S(12)	2.4797(10)
In(2)	S(21)	2.4333(11)
In(2)	S(21)	2.4334(11)
In(2)	S(22)	2.4841(11)
In(2)	S(22)	2.4841(11)
Ag(1)	P(1)	2.4574(10)
Ag(1)	P(1)	2.4574(10)
Ag(1)	S(12)	2.6906(10)
Ag(1)	S(12)	2.6907(10)
Ag(2)	P(2)	2.4527(10)
Ag(2)	P(2)	2.4527(10)
Ag(2)	S(22)	2.6797(10)
Ag(2)	S(22)	2.6797(10)
S(11)	C(11)	1.824(4)
S(12)	C(12)	1.830(5)
S(21)	C(21)	1.816(4)
S(22)	C(22)	1.834(4)
P(1)	C(121)	1.819(4)
P(1)	C(111)	1.824(4)
P(1)	C(131)	1.827(4)
P(2)	C(231)	1.822(4)
P(2)	C(211)	1.823(4)
P(2)	C(221)	1.824(4)
C(114)	C(113)	1.374(6)
C(114)	C(115)	1.378(5)
C(112)	C(113)	1.375(6)
C(112)	C(111)	1.392(5)
C(111)	C(116)	1.392(5)
C(115)	C(116)	1.391(5)

Atom 1	Atom 2	Distance
C(121)	C(122)	1.390(6)
C(121)	C(126)	1.407(5)
C(122)	C(123)	1.393(5)
C(123)	C(124)	1.380(6)
C(124)	C(125)	1.375(7)
C(125)	C(126)	1.384(5)
C(131)	C(132)	1.379(5)
C(131)	C(136)	1.390(5)
C(132)	C(133)	1.392(5)
C(133)	C(134)	1.355(6)
C(134)	C(135)	1.383(6)
C(135)	C(136)	1.376(5)
C(211)	C(216)	1.386(5)
C(211)	C(212)	1.387(5)
C(212)	C(213)	1.384(6)
C(213)	C(214)	1.385(6)
C(214)	C(215)	1.387(6)
C(215)	C(216)	1.388(5)
C(221)	C(226)	1.394(5)
C(221)	C(222)	1.398(5)
C(222)	C(223)	1.380(5)
C(223)	C(224)	1.390(5)
C(224)	C(225)	1.379(5)
C(225)	C(226)	1.385(5)
C(231)	C(232)	1.387(5)
C(231)	C(236)	1.392(5)
C(232)	C(233)	1.396(5)
C(233)	C(234)	1.371(6)
C(234)	C(235)	1.383(6)
C(235)	C(236)	1.382(5)

Crystal Data and Data Collection Parameters for $C_{40}H_{42}AgInP_2S_4$

formula	$C_{40}H_{42}AgInP_2S_4$
formula weight	935.67
space group	P2/c (No. 13)
a, A	15.6671(4)
b, A	12.6092(4)
c, A	21.6432(8)
β, deg	108.412(2)
V, A^3	4056.7(4)
Z	4
d_{calc}, g cm^{-3}	1.532
crystal dimensions, mm	0.28×0.19×0.09
temperature, K	150.0
radiation (wavelength)	MO K_α(0.71073A)
monochromator	graphite
linear abs coef, mm^{-1}	1.340
absorption correction applied	empirical[a]
transmission factors: min, max	0.72, 0.89
diffractometer	Nonius Kappa CCD
h, k, l range	0 to 20; 0 to 16; –28 to 27
2θ range, deg	4.24 to 55.79
mosaicity, deg	0.37
programs used	SHELXL-97
F_{000}	1888.0
weighting	$1/[\sigma^2(Fo^2) + (0.0299P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$
data collected	32849
unique data	9649
R_{int}	0.087
data used in refinement	9646
cutoff used in R-factor calculations	$F_o^2 > 2.0\sigma(F_o^2)$
data with $I > 2.0\sigma(I)$	5328
number of variables	439
largest shift/esd in final cycle	0.00
$R(F_o)$	0.039
$R_w(F_o^2)$	0.076
goodness of fit	0.857

[a]Otwinowski, Z. and Minor, W., Methods Enzymol., **1996**, 276, 307.

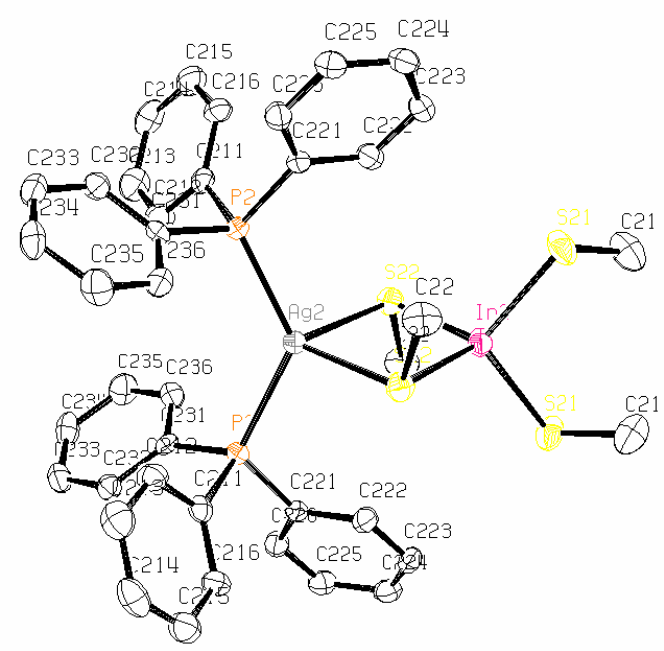


Table of Bond Angles in Degrees for $C_{40}H_{42}AgInP_2S_4$

Numbers in parentheses are estimated standard deviations in the least significant digits.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S(11)	In(1)	S(11)	111.83(6)	C(211)	P(2)	Ag(2)	113.79(11)
S(11)	In(1)	S(12)	107.26(3)	C(221)	P(2)	Ag(2)	113.86(12)
S(11)	In(1)	S(12)	115.13(4)	C(113)	C(114)	C(115)	119.9(4)
S(11)	In(1)	S(12)	115.13(4)	C(113)	C(112)	C(111)	119.8(4)
S(11)	In(1)	S(12)	107.26(3)	C(114)	C(113)	C(112)	121.1(4)
S(12)	In(1)	S(12)	99.87(5)	C(112)	C(111)	C(116)	119.1(4)
S(21)	In(2)	S(21)	108.91(5)	C(112)	C(111)	P(1)	119.1(3)
S(21)	In(2)	S(22)	108.80(3)	C(116)	C(111)	P(1)	121.8(3)
S(21)	In(2)	S(22)	114.84(4)	C(114)	C(115)	C(116)	119.7(4)
S(21)	In(2)	S(22)	114.85(4)	C(115)	C(116)	C(111)	120.4(3)
S(21)	In(2)	S(22)	108.80(3)	C(122)	C(121)	C(126)	118.5(4)
S(22)	In(2)	S(22)	100.64(5)	C(122)	C(121)	P(1)	125.3(3)
P(1)	Ag(1)	P(1)	127.63(5)	C(126)	C(121)	P(1)	116.1(3)
P(1)	Ag(1)	S(12)	105.85(3)	C(121)	C(122)	C(123)	120.5(4)
P(1)	Ag(1)	S(12)	110.64(3)	C(124)	C(123)	C(122)	120.1(4)
P(1)	Ag(1)	S(12)	110.64(3)	C(125)	C(124)	C(123)	120.0(4)
P(1)	Ag(1)	S(12)	105.85(3)	C(124)	C(125)	C(126)	120.6(4)
S(12)	Ag(1)	S(12)	89.71(4)	C(125)	C(126)	C(121)	120.1(4)
P(2)	Ag(2)	P(2)	128.40(5)	C(132)	C(131)	C(136)	118.6(4)
P(2)	Ag(2)	S(22)	112.32(3)	C(132)	C(131)	P(1)	124.4(3)
P(2)	Ag(2)	S(22)	103.31(3)	C(136)	C(131)	P(1)	117.0(3)
P(2)	Ag(2)	S(22)	103.30(3)	C(131)	C(132)	C(133)	119.9(4)
P(2)	Ag(2)	S(22)	112.32(3)	C(134)	C(133)	C(132)	120.7(4)
S(22)	Ag(2)	S(22)	91.03(5)	C(133)	C(134)	C(135)	120.4(4)
C(11)	S(11)	In(1)	101.02(14)	C(136)	C(135)	C(134)	119.1(4)
C(12)	S(12)	In(1)	102.06(15)	C(135)	C(136)	C(131)	121.4(4)
C(12)	S(12)	Ag(1)	107.93(14)	C(216)	C(211)	C(212)	118.9(4)
In(1)	S(12)	Ag(1)	85.21(3)	C(216)	C(211)	P(2)	122.8(3)
C(21)	S(21)	In(2)	99.95(14)	C(212)	C(211)	P(2)	118.4(3)
C(22)	S(22)	In(2)	101.74(14)	C(213)	C(212)	C(211)	120.9(4)
C(22)	S(22)	Ag(2)	113.59(15)	C(212)	C(213)	C(214)	120.3(4)
In(2)	S(22)	Ag(2)	84.16(3)	C(213)	C(214)	C(215)	119.0(4)
C(121)	P(1)	C(111)	106.40(19)	C(214)	C(215)	C(216)	120.7(4)
C(121)	P(1)	C(131)	104.77(17)	C(211)	C(216)	C(215)	120.3(4)
C(111)	P(1)	C(131)	102.62(17)	C(226)	C(221)	C(222)	118.8(3)
C(121)	P(1)	Ag(1)	111.49(12)	C(226)	C(221)	P(2)	122.9(3)
C(111)	P(1)	Ag(1)	116.19(12)	C(222)	C(221)	P(2)	118.3(3)
C(131)	P(1)	Ag(1)	114.30(13)	C(223)	C(222)	C(221)	120.2(4)
C(231)	P(2)	C(211)	103.73(17)	C(222)	C(223)	C(224)	120.6(4)
C(231)	P(2)	C(221)	102.71(16)	C(225)	C(224)	C(223)	119.5(4)
C(211)	P(2)	C(221)	104.26(18)	C(224)	C(225)	C(226)	120.4(4)
C(231)	P(2)	Ag(2)	116.98(13)	C(225)	C(226)	C(221)	120.5(3)
C(232)	C(231)	C(236)	119.1(3)	C(234)	C(233)	C(232)	120.5(4)
C(232)	C(231)	P(2)	122.4(3)	C(233)	C(234)	C(235)	119.9(4)
C(236)	C(231)	P(2)	118.5(3)	C(236)	C(235)	C(234)	120.2(4)
C(231)	C(232)	C(233)	119.9(4)	C(235)	C(236)	C(231)	120.4(4)

Synthetic Procedure

A 500 ml 3 neck flask is charged with NaSEt in anhydrous methanol. $InCl_3$ (1.92 g, 10.9 mmol) is rapidly added, resulting in a clear solution (on some occasions small white flocculent ppt is also observed). The mixture is stirred and allowed react for 15 to 30 minutes. In a second flask, a solution, or suspension of anhydrous CuCl (Aldrich) (3.11 g, 3.82 mmol), and PPh_3 (3.11 g, 3.82 mmol), in a mixture of anhydrous CH_3CN/CH_2Cl_2 (3:1 volume ratio), is rapidly added to $Na^+[In(SEt)_4]^-$ (formed *in situ*). After 24 hours the reaction is concentrated and the product extracted (200 mL of desired solvent) and filtered through Celite. Evaporation of the solvent affords the pale yellow precursor. A similar preparative route is used for the preparation of the Ag analogues, but in the absence of light.

Selective NMR and Analysis Data

For **1**[$\{PPh_3\}_2Cu(SEt)_2In(SEt)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 1.24 ppm (t); δ 2.67 ppm (q); δ 7.33 ppm (m): Elemental Analysis by Galbraith Labs, Knoxville, TN 37921. Calc. for **1** (%), C 55.78, H 5.32; Found (%) C 55.61, H 5.21

For **2** [$\{PPh_3\}_2Cu(SePh)_2In(SePh)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 6.89 ppm (s); δ 7.02 ppm (d); δ 7.26 ppm (br d), δ 7.37 ppm (m): Elemental Analysis by Galbraith Labs, Knoxville, TN 37921. Calc. for **3** (%), C 54.30, H 3.80; Found (%) C 54.57, H 3.73

For **3** [$\{PBu_3\}_2Cu(SEt)_2In(SEt)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 2.76 ppm (q); δ 1.56 ppm (br m); δ 1.43 ppm (br m); δ 1.33 ppm (t); δ 0.94 ppm (t)

For **4** [$\{PPh_3\}_2Cu(SMe)_2In(SMe)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 2.12 ppm (s); δ 7.31 ppm (br s): Elemental Analysis by Galbraith Labs, Knoxville, TN 37921. Calc. for **4** (%), C 53.90, H 4.75; Found (%) C 53.73, H 4.53

For **5** [$\{PBu_3\}_2Cu(SePh)_2In(SePh)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 0.86 ppm (t); δ 1.32 ppm (br s); δ 7.07 ppm (m), δ 7.50 ppm (br s)

For **6** [$\{PPh_3\}_2Ag(SMe)_2In(SMe)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 7.33 ppm (br m); δ 2.12 ppm (s): Elemental Analysis by Galbraith Labs, Knoxville, TN 37921. Elemental Analysis Calc. for **6** (%), C 51.35, H 4.52; Found (%) C 51.62, H 4.59

For **7** [$\{PBu_3\}_2Ag(SEt)_2In(SEt)_2$]: ^1H NMR: 300 MHz; $CDCl_3$; δ 0.90 ppm (t); δ 1.30 ppm (t); δ 1.41 ppm (br s); δ1.61 ppm (br s); δ2.74 ppm (q)

Selective EDAX Analysis Data

EDAX data for SSP **3** to afford $CuInS_2$

Element	Wt%	At%	K-Ratio	Z	A	F
S K	25.58	49.12	0.1879	1.1233	0.6447	1.0143
In K	49.06	26.30	0.3958	0.9092	0.8874	1.0000
Cu K	25.36	24.58	0.2404	1.0028	0.9451	1.0000
Total	100.00	100.00				
Element	**Net Inte.**	**Bkgd Inte.**	**Inte. Error**	**P/B**		
S K	103.78	5.70	0.87	18.20		
In K	69.72	4.56	1.07	15.28		
Cu K	34.65	2.38	1.52	14.58		
Total	100.00	100.00				

EDAX data for SSP **7** to afford $AgIn_5S_8$

Element	Wt %	At %*	K-Ratio	Z	A	F
S K	25.60	54.79	0.2063	1.1393	0.6906	1.0245
Ag K	19.31	12.29	0.1558	0.9455	0.8532	1.0000
In K	55.09	32.93	0.4671	0.9264	0.9152	1.0000
Total	100.00	100.00				
Element	**Net Inte.**	**Bkgd Inte.**	**Inte. Error***	**P/B**		
S K	15.44	1.93	2.85	8		
In K	3.98	2.60	7.62	1.53		
Cu K	11.09	2.93	3.71	3.78		
Total	100.00	100.00				

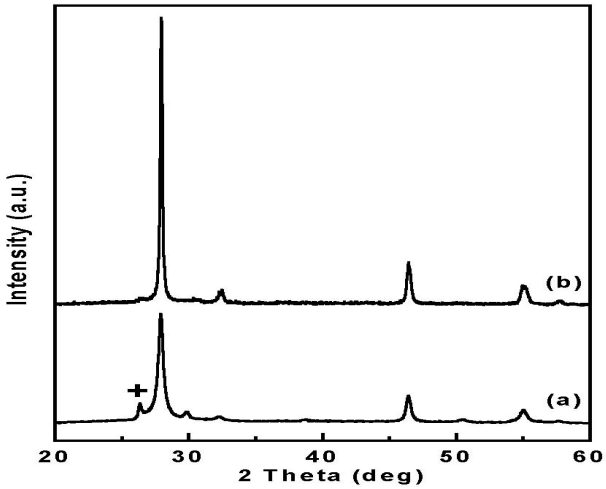
*overlapping bands hinder exact deciphering At/Wt %

Thermal DATA: TGA and DSC

Single Source Precursors $[\{L\}_2Cu(ER)_2M(ER)_2]$	TGA			DSC	
	Onset °C	MRW** °C	Residue %	M.P. °C	Dec. °C
1 $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$	236	269	25	122	266
2 $[\{PPh_3\}_2Cu(SePh)_2In(SePh)_2]$	223	253	22	53	219
3 $[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$	189	238	27	--	264
4 $[\{PPh_3\}_2Cu(SMe)_2In(SMe)_2]$	221	254	27	164	242
5 $[\{PBu_3\}_2Cu(SePh)_2In(SePh)_2]$	229	255	26	*	*
6 $[\{PPh_3\}_2Ag(SMe)_2In(SMe)_2]$	229	272	29	141	238
7 $[\{PBu_3\}_2Ag(SEt)_2In(SEt)_2]$	187	239	30	--	285

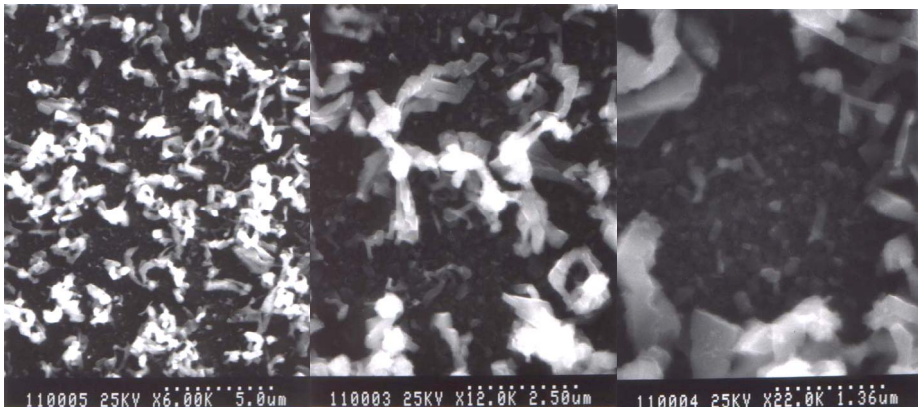
*not recorded
**if more then one MRW, then max. value listed

XRD Pattern Data

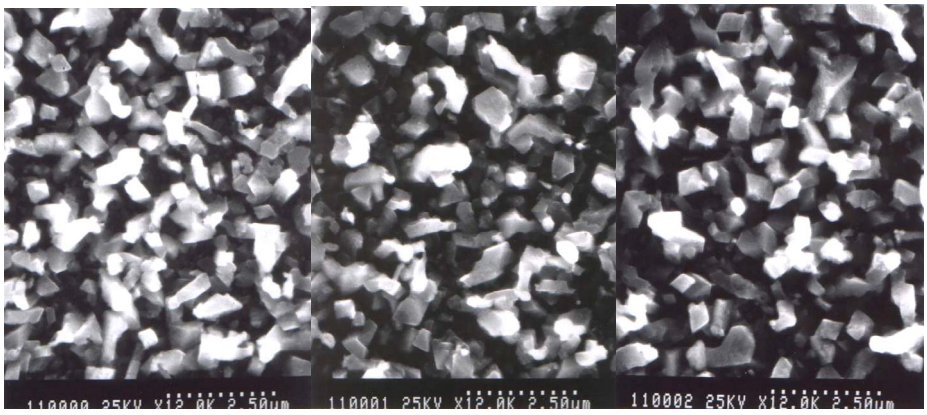


XRD Data of the CuInS2 film grown in the cold-wall reactor at 400 °C.
(a) as-grown and (b) after annealing at 600 °C for 10 min under N_2 flow from SSP **3**.

SEM Images for Deposited $AgIn_5S_8$ Polycrystalline Thin Films Using SSP 7.



Films grown at 400 °C.



Films grown at 450 °C.

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13. ABSTRACT ***(Maximum 200 words)***

We report a new simplified synthetic procedure for commercial manufacture of ternary single source precursors (SSP). This new synthetic process has been successfully implemented to fabricate known SSPs on bulk scale and the first liquid SSPs to the semiconductors $CuInSe_2$ and $AgIn_xS_y$. Single crystal X-ray determination reveals the first unsolvated ternary AgInS SSP. SSPs prepared via this new route have successfully been used in a spray assisted chemical vapor deposition (CVD) process to deposit polycrystalline thin films, and for preparing ternary nanocrystallites.

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